

# OCCURRENCE OF POLYBROMINATED DIPHENYL ETHERS (PBDES) IN MARINE SEDIMENTS AND SHELLFISH TISSUE FROM THE CENTRAL BASIN OF PUGET SOUND

## Scott Mickelson, King County Marine and Sediment Assessment Group

### Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants and can enter the environment from both point and nonpoint sources. These compounds have increasingly come under scrutiny for their potential environmental and human health effects. King County began studying PBDEs in the marine environment in 2006, looking first at their distribution in marine sediments and, then, their distribution in shellfish tissue.

Marine sediment samples have been collected from several areas throughout Puget Sound: at the County's West Point Wastewater Treatment Plant outfall; at the location of the future Brightwater Wastewater Treatment Plant outfall; and at ambient locations in the Main Basin, Elliott Bay, and three smaller, shallow embayments. Butter clams (*Saxidomus giganteus*) are routinely collected twice a year, in March and August, from nine locations within King County (a tenth location has been added in 2010).

PBDE analysis is performed using ultra-sonic solvent extraction with analysis by gas chromatography and inductively coupled plasma mass spectroscopy (GC/ICPMS). The following 14 PBDE congeners are quantified: TriBDE-17, TriBDE-28, TetraBDE-47, TetraBDE-66, TetraBDE-71, PentaBDE-85, PentaBDE-99, PentaBDE-100, HexaBDE-138, HexaBDE-153, HexaBDE-154, HeptaBDE-183, HeptaBDE-190, and DecaBDE-209.

### Marine Sediments

Figures 1a and 1b show the locations of King County's routine ambient sediment monitoring locations. The 14 stations shown in blue on Figure 1a were initially sampled for PBDEs in 2007. The eight Elliott Bay stations shown in Figure 1b are sampled on a 2-year cycle and were sampled again in 2009. The remaining ambient sediment monitoring stations will be sampled on a 5-year cycle, next sampled in 2012.

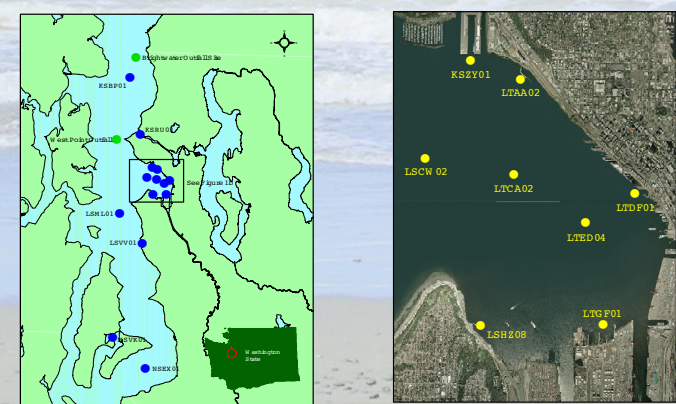


Figure 1a

Figure 1b

Figure 1a also shows, in green, the locations of the West Point and Brightwater treatment plant outfalls. Samples were collected from nine stations at West Point in 2006. Samples were collected from 11 stations at Brightwater in both 2006 and 2007. All of the treatment plant samples were analyzed for PBDEs as part of the overall analytical suite. All sediment samples collected for PBDE analysis have been collected from the 0- to 2-cm depth stratum, employing modified, 0.1 m<sup>2</sup> van Veen grab samplers, deployed from King County's research vessel, *Liberty*.

Contact Information  
Scott Mickelson  
King County DNR  
201 S. Jackson St. #600  
Seattle, WA 98104  
206.296.8247 phone  
206.296.0192 fax  
[scott.mickelson@kingcounty.gov](mailto:scott.mickelson@kingcounty.gov)



### Results for Marine Sediments

Figure 2a shows the range of PBDE concentrations from the initial ambient sediment sampling event in June 2007. The reported PBDE concentration is the sum of the 14 congeners analyzed, in micrograms per kilogram on a dry weight basis (mg/Kg DW). The figure bands the results into three main categories: the three deep, depositional Central Basin stations, the eight Elliott Bay stations, and the three shallow embayment stations. Concentrations ranged from 1.23 mg/Kg DW at the Central Basin station located near Point Jefferson (KSBP01) to 14.5 mg/Kg DW at the station located in outer Salmon Bay (KSRU03). Station KSRU03 is located on the marine side of the Hiram Chittenden locks and receives a high degree of commercial and recreational vessel traffic. This may account for the higher PBDE concentration, since these compounds are found in many types of boat equipment, including personal flotation devices, cushions, fenders, and electronics. Figure 2b shows the PBDE concentrations detected at the eight Elliott Bay stations during both the 2007 and 2009 sampling events. PBDE concentrations in Elliott Bay have ranged from 2.82 to 10.5 mg/Kg DW.

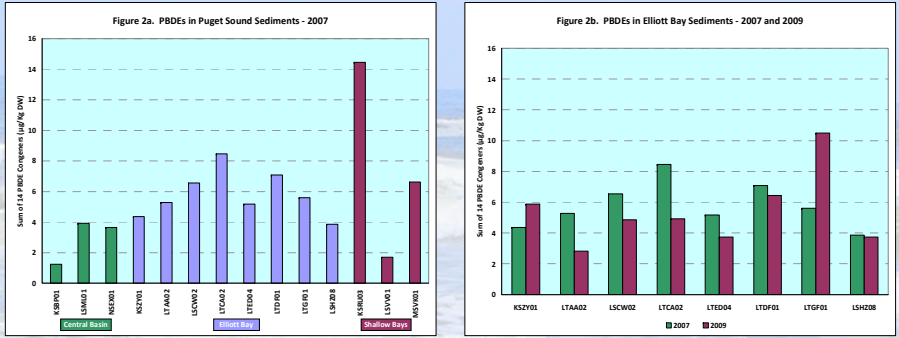


Figure 3 shows all sediment PBDE data collected to date. King County collected PBDE samples from 9 stations proximal to its West Point wastewater treatment plant outfall in 2006 and from 11 stations at the site of its future Brightwater wastewater treatment plant outfall in both 2006 and 2007. Mean PBDE concentrations (+/- 1 SD) for the West Point and Brightwater sites are compared to mean values for the three deep Central Basin stations (KSPB01, LSML01, NSEX01) and the Elliott Bay stations, as well as the single values for Outer Salmon Bay (KSRU03), Fauntleroy Cove (LSVV01), and Quartermaster Harbor (MSVK01). The Brightwater site is a deep, depositional area – comparable to the other three Central Basin stations. Both West Point and Fauntleroy Cove are high-energy environments, with little deposition of fine material.

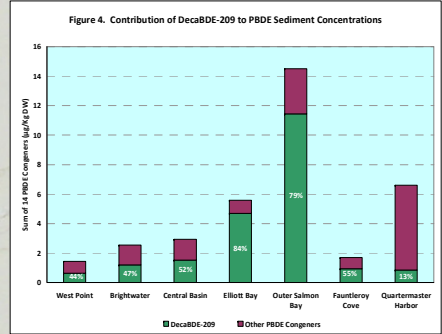


Figure 4 shows the average contribution of DecaBDE-209 to each of the PBDE concentrations shown in Figure 3. Overall, the Elliott Bay samples exhibited the highest contribution of DecaBDE-209, ranging from 70 to 98% (mean 84%) of the measured PBDE concentration. The low DecaBDE-209 contribution of 13% in the sample collected from Quartermaster Harbor may be due to photolytic debromination of this congener to another, lesser-brominated congener. The Quartermaster Harbor sediment sample was collected from a shallow depth of approximately seven meters.

### Shellfish Tissue

Figure 5 shows the locations of King County's routine shellfish monitoring stations. Butter clam samples for PBDE analysis were collected from nine of these locations in March and August of 2008 and 2009. A new station, located in Quartermaster Harbor at Burton Acres Park, was added to the program in 2010. Each tissue sample consists of the soft body parts of a minimum of five clams between 60 to 120 mm in size. Prior to opening the clams in the lab,

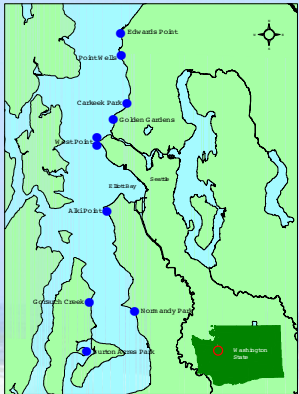


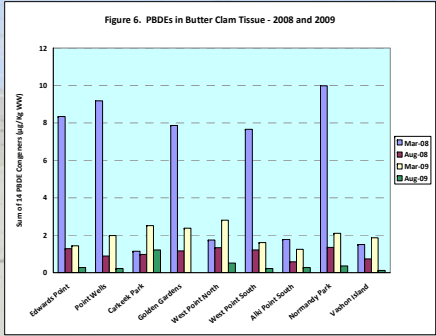
Figure 5



the shells are rinsed with deionized water to remove sand and adhering material. Each clam is measured and the length recorded. Tissues from the clams are removed with ceramic knives and composited with their liquor. The tissues and liquor are homogenized in a blender equipped with stainless steel blades and stored frozen until analysis. PBDEs in clam samples are also analyzed by ultra-sonic solvent extraction with GC/ICPMS instrumentation.

### Results for Shellfish Tissue

Nine of the 14 PBDE congeners were detected in butter clam tissue samples. TriBDE-17, TriBDE-28, TetraBDE-66, HexaBDE-138, and HeptaBDE-183 were not detected in any of the 35 samples analyzed. Figure 6 presents the range of PBDE concentrations detected over the four sampling events, shown in micrograms per kilogram on a wet basis (mg/Kg WW). PBDE concentrations at all stations have been higher in the samples collected in March than in those collected in August. The elevated PBDE concentration detected at five stations during the March 2008 sampling event were not evident during other sampling events. Lipid normalization of the results does not alter the distribution of results significantly. The five elevated concentrations ranged from 7.65 to 9.97 mg/Kg WW. All other detected PBDE concentrations ranged from 0.12 to 2.79 mg/Kg WW. Unlike sediment



samples, DecaBDE-209 was not the predominant congener detected in shellfish tissue samples. DecaBDE-209 was detected in only 7 out of 35 samples, all at very low levels. The predominant congeners detected in shellfish tissue samples were TetraBDE-47 and TetraBDE-71, which, together, comprised between 39 and 100% of the PBDE concentration in all of the samples. Of those two congeners, TetraBDE-71 was generally detected at the higher concentration.

Figure 7 shows the distribution of TetraBDE-71, TetraBDE-47, PentaBDE-99, and the sum of the other six detected congeners from the March 2007 sampling event. In the five samples with elevated PBDE concentrations, TetraBDE-71 represented 87 to 97% of the PBDE sum. In the other four samples, TetraBDE-71 represented 53 to 70% of the PBDE sum.

